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(54) Title: PROCESSES FOR OXIDATION OF BROMIDES TO PRODUCE BROMINE AND CATALYSTS USEFUL THEREIN

(57) Abstract: Methods are provided for producing bromine wherein an aqueous solution is formed from at least a bromide source, an oxidant, and a catalyst comprising a Group 1 cation and an oxide of a transition metal.

PROCESSES FOR OXIDATION OF BROMIDES TO PRODUCE BROMINE AND CATALYSTS USEFUL THEREIN

BACKGROUND

[0001] Bromine is used in a wide range of industries. For example, bromine is used in the manufacture of flameproofing agents, 1,2-dibromoethane ($\text{CH}_2\text{BrCH}_2\text{Br}$) (which is used as a petrol additive to prevent lead being deposited in cylinders), compounds used in photography (e.g. silver bromide, AgBr , which is the light sensitive material in film), dyestuffs and drugs; in the analytical laboratory in testing for unsaturation in organic compounds, where bromine adds across the multiple bonds of unsaturated compounds, as a disinfectant; and in making fumigants, water purification compounds, dyes, medicinals; and sanitizers. Bromine can be produced by oxidation of bromides using hydrogen peroxide as the oxidant. For example, the following reaction is suitable: $\text{H}_2\text{O}_2 + 2\text{HBr} \longrightarrow \text{Br}_2 + 2\text{H}_2\text{O}$ (Reaction (1)). Bromine can also be produced by oxidation of bromides using chlorine as the oxidant. For example, the following reaction is suitable: $2\text{NaBr} + \text{Cl}_2 \rightleftharpoons \text{Br}_2 + 2\text{NaCl}$ (Reaction (2)).

[0002] US 5,266,295 describes use of a strong acid, such as sulfuric or phosphoric acid, to improve effectiveness when hydrogen bromide is oxidized to bromine using hydrogen peroxide as the oxidant. However, process economics are affected by the addition of an acid; and in some cases an acid source is not readily available. Each of Reactions (1) and (2) could benefit from the addition of catalysts to increase the percent conversion of bromide to bromine. Ammonium molybdate ($(\text{NH}_4^+)_2\text{MoO}_4^-$) is a known oxidation catalyst to allow iodometric titration of H_2O_2 . However, NH_4^+ is not a cation of choice for use as an additive in a commercial bromine tower.

[0003] Thus in spite of currently available technologies, a need remains for commercially feasible methods that provide increased percent conversion when oxidizing bromides to produce bromine, and catalysts for use therein.

THE INVENTION

[0004] This invention meets the above-described need by providing methods for producing bromine comprising forming an aqueous solution from at least a bromide source, an oxidant, and a catalyst comprising a Group 1 cation and an oxide of a transition metal. Further provided are methods comprising (i) forming an aqueous solution from at least a bromide source, an oxidant, a mineral acid, and a catalyst

comprising a Group 1 cation and an oxide of a transition metal, wherein the aqueous solution has a pK_a of less than about -1.74; and (ii) producing bromine. Also provided are methods for producing bromine comprising forming an aqueous solution from at least a bromide source, an oxidant, hydrogen chloride, and a catalyst according to this invention. Methods according to this invention can be conducted in continuous mode or batch mode. This invention also provides such methods for producing bromine wherein the aqueous solution has a pK_a that is less than about -1.74.

Catalysts

[0005] Catalysts used in methods according to this invention comprise a Group 1 cation and an anion comprising a transition metal anion. The Group 1 cation can comprise Na^+ , K^+ , Rb^+ , Cs^+ , Fr^+ , Li^+ , or H^+ . The anion can comprise an oxide derived from one or more transition metals such as vanadium, cerium, chromium, manganese, niobium, molybdenum, ruthenium, tungsten, rhenium, and/or osmium. For example, the anion can comprise MoO_4^{2-} . An example catalyst according to this invention comprises sodium molybdate (Na_2MoO_4). Catalysts that comprise transition metal oxide anions that are capable of promoting the decomposition of hydrogen peroxide are useful in methods of this invention as are catalysts wherein the anion is capable of activating hydrogen peroxide toward oxidation of bromide, such that bromine is obtained in at least 90 wt% (or at least 95 wt% or 98 wt%) hydrogen peroxide-based yield.

Bromide Sources

[0006] In methods of this invention, the bromide source can comprise hydrogen bromide (HBr) or sodium bromide (NaBr). The HBr can be generated in situ from decomposition of less stable (such as secondary and tertiary) aliphatic alkyl bromides. Other suitable bromide sources comprise potassium bromide (KBr) and lithium bromide (LiBr). Another bromide source suitable for this invention comprises aqueous hydrobromic acid, hydrogen bromide gas, or a Group 1 metal bromide in combination with hydrochloric acid. Group 1 metals include lithium (Li), sodium (Na), and potassium (K).

Oxidants

[0007] In methods of this invention, the oxidant can comprise hydrogen peroxide (H_2O_2), chlorine (Cl_2), or oxygen (O_2). The oxidant can comprise a salt of hydrogen peroxide, e.g., lithium peroxide. Chlorine as an oxidant can be introduced as a gas or generated in situ, from chloride ion and peroxides, including hydrogen peroxide. Oxygen, an economically advantageous oxidant of bromide ion, typically requires temperatures higher than ambient temperature for activation, yet it can be used in gaseous form. Oxygen transporters such as cerium oxide or vanadium pentoxide can be used. Other suitable oxidants comprise organic peroxides, e.g. benzoyl peroxide, which decompose upon heating.

Mineral Acids

[0008] In methods of this invention, the mineral acid can enhance acidity of the aqueous solution that is formed. Suitable mineral acids include hydrochloric acid, sulfuric acid and/or phosphoric acid.

Oxidation of Bromides to Bromine

[0009] Oxidation of bromides to bromine according to this invention typically takes place in a commercial setting in a packed column with addition of the reagents and steam in a continuous system using hydrogen peroxide as an oxidant for bromine production; however, variations are possible as will be familiar to those skilled in the art.

[0010] This invention provides that bromine can be derived from about 0.01 wt% to about 60 wt% HBr, about 3 wt% to about 70 wt% H_2O_2 , about 0.03 wt% to about 0.5 wt% catalyst according to this invention and about 5 wt% to about 20 wt% HCl, all based on the sum of the weights of the HBr, the H_2O_2 , the catalyst, and the HCl prior to each being used in the bromine derivation. Typically, the bromide source, the oxidant, and the catalyst, and when included, the hydrogen chloride or mineral acid, are in aqueous solution. This invention also provides that the molar ratio of bromide source to catalyst according to this invention can be from about 150:1 to about 1200:1, or about 200:1 to about 1000:1, or about 400:1 to about 900:1, or about 600:1 to about 850:1, or about 658:1 to about 831:1.

Examples

[0011] The following examples are illustrative of the principles of this invention. It is understood that this invention is not limited to any one specific embodiment exemplified herein.

[0012] Example 1: HBr (357.20 g of 7.46 wt% aqueous solution; 0.33 mol HBr) and Na_2MoO_4 (2.04 g of 4 wt% aqueous solution; 0.4 mmol Na_2MoO_4) were added into a 500 mL Erlenmeyer flask along with HCl (16.08 g of 12M HCl; 0.13 mol HCl) and H_2O_2 (2.84 g of 70 wt% aqueous solution; 0.06 mol H_2O_2). The mixture was stirred, cooled, and kept at 15 - 20°C during addition at 10 mL/min into the reflux stream above a 12" x 1" column fitted with 24/40 glassware into a 500 mL three necked round bottomed flask into which live steam was injected. Excess condensate and HBr were removed by pump and the overhead products, comprising bromine and water, were condensed using a Friedrich's condenser cooled with aqueous glycol at 4 - 7°C. This condensate and any uncondensables were conveyed into 300 mL (15 wt%) Na_2SO_3 solution where the bromine was reduced into bromide ion and quantified by titration with 0.1N AgNO_3 . A total of 9.27 g bromine was obtained; a H_2O_2 -based bromine yield of 99.04 wt%.

[0013] Example 2: The procedure of Example 1 was used with HBr (356.77 g of 8.96 wt% aqueous solution; 0.40 mol HBr), HCl (11.40 g of 12M HCl; 0.09 mol HCl), Na_2MoO_4 (3.09 g of 4 wt% aqueous solution; 0.6 mmol Na_2MoO_4), and H_2O_2 (2.91 g of 70 wt% aqueous solution; 0.06 mol H_2O_2). A total of 8.99 g bromine was obtained; a H_2O_2 -based bromine yield of 93.91 wt%.

[0014] Example 3 (Comparative Example): The procedure of Example 1 was used with HBr (356.54 g of 7.52 wt% aqueous solution; 0.33 mol HBr), HCl (17.90 g of 12M HCl; 0.15 mol HCl), and H_2O_2 (2.80 g of 70 wt% aqueous solution; 0.06 mol H_2O_2). No catalyst according to this invention was added. A total of 7.32 g bromine was obtained; a H_2O_2 -based bromine yield of 79.38 wt%.

[0015] Example 4 (Comparative Example): The procedure of Example 1 was used with HBr (360.80 g of 6.19 wt% aqueous solution; 0.28 mol HBr), HCl (19.27g of 12M HCl; 0.16 mol HCl), and H_2O_2 (3.39 g of 70% wt aqueous solution; 0.07 mol H_2O_2) added into the feed HBr. No catalyst according to this invention was added. A total of 5.19 g bromine was obtained; a H_2O_2 -based bromine yield of 46.43 wt.

[0016] Example 5 (Comparative Example): The procedure of Example 1 was used with HBr (355.68 g of 7.46 wt% aqueous solution; 0.33 mol HBr), HCl (159.02g of 30 wt% aqueous solution; 1.14 mol HCl), and H_2O_2 (2.65g of 70 wt% aqueous solution;

0.06 mol H₂O₂). No catalyst according to this invention was added. A total of 8.30 g bromine was obtained; a H₂O₂-based bromine yield of 95.09 wt%.

[0017] Example 6 (Comparative Example: The procedure of Example 1 was used with HBr (356.65 g of 17.20 wt% aqueous solution; 0.76 mol HBr), HCl (22.04 wt% by titration; 46.10g (0.28mol) HCl), and H₂O₂ (14.98 g of 70 wt% aqueous solution; 0.31 mol H₂O₂); in addition, a recycle acid source was used. No catalyst according to this invention was added. A total of 45.65 g bromine was obtained; a H₂O₂-based bromine yield of 92.50 wt%.

[0018] As can be see from these examples (data summarized in Table 1), use of a catalyst of this invention in a bromine oxidation reaction improves Br₂ yield. Compare the oxidation reaction of Example 3, where 0.33 mol HBr were oxidized using 0.15 mol HCl and 0.06 mol H₂O₂, resulting in a H₂O₂-based Br₂ yield of 79.38 wt%, to the reaction of Example 1, where 0.33 mol HBr were oxidized using 0.13 mol HCl, 0.06 mol H₂O₂, and 0.4 mmol of a catalyst according to this invention (Na₂MoO₄), resulting in a H₂O₂-based Br₂ yield of 99.04 wt% (vs. the 79.38 wt% yield of Example 3). Also compare Example 3 to Example 2, where slightly less HCl was used (0.09 mol vs. 0.15 mol), and 0.6 mmol of a catalyst according to this invention (Na₂MoO₄) was used, resulting in a H₂O₂-based Br₂ yield of 93.91 wt% (vs. the 79.38 wt% yield of Example 3). The Examples also show that increased amounts of HCl can improve the effectiveness in a bromine oxidation reaction. For example, comparing Example 3 to Example 5, increasing HCl from 0.15 mol to 1.14 mols can result in increased oxidant-based bromine (Br₂) yield from 79.38 wt% to 95.09 wt%.

Table 1

Example Number	HBr (mols)	HCl (mols)	H ₂ O ₂ (mols)	Na ₂ MoO ₄ (mmols)	H ₂ O ₂ -based Br ₂ yield (wt%)
1	0.33	0.13	0.06	0.4	99.04
2	0.40	0.09	0.06	0.6	93.91
3	0.33	0.15	0.06	----	79.38
4	0.28	0.16	0.07	----	46.43
5	0.33	1.14	0.06	----	95.09
6	0.76	0.28	0.31	----	92.50

[0019] While the present invention has been described in terms of one or more preferred embodiments, it is to be understood that other modifications may be made without departing from the scope of the invention, which is set forth in the claims below.

CLAIMS

We Claim:

1. A method for producing bromine comprising forming an aqueous solution from at least a bromide source, an oxidant, and a catalyst comprising a Group 1 cation and an oxide of a transition metal.
2. A method according to Claim 1 wherein the Group 1 cation comprises Na⁺ or K⁺.
3. A method according to Claim 1 wherein the oxide comprises molybdate (MoO₄⁻²).
4. A method according to Claim 1 wherein the catalyst comprises sodium molybdate (Na₂MoO₄).
5. A method according to Claim 1 wherein the bromide source comprises hydrogen bromide or sodium bromide.
6. A method according to Claim 1 wherein the oxidant comprises hydrogen peroxide (H₂O₂), chlorine (Cl₂), or oxygen (O₂).
7. A method according to Claim 4 wherein the molar ratio of bromide source to catalyst is from about 150:1 to about 1200:1.
8. A method comprising:
 - (i) forming an aqueous solution from at least a bromide source, an oxidant, a mineral acid, and a catalyst comprising a Group 1 cation and an oxide of a transition metal, wherein the aqueous solution has a pK_a of less than about -1.74; and
 - (ii) producing bromine.
9. A method for producing bromine comprising forming an aqueous solution from at least hydrogen bromide, sodium molybdate, hydrogen peroxide and HCl.

10. A method for producing bromine comprising forming an aqueous solution from at least a bromide source, an oxidant, a mineral acid, and a catalyst comprising a Group 1 cation and an oxide of a transition metal.